

Theoretical analysis of reaction-diffusion process in biocatalyst modified electrodes: Solutions derived via Akbari-Ganji method and Taylor's series with Ancient Chinese algorithms

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The mathematical modelling of bio-catalytically active chemically modified electrodes, including redox enzymes, is discussed. This model is created on a system of nonlinear reaction-diffusion equations with the Michaelis-Menten kinetics of an enzyme reaction. The present report uses the effective analytical methods known as the latest Akbari-Ganji method and Taylor's series with Ancient Chinese algorithms to solve the nonlinear system. Various parameters and their effects on current density are explored. The concentration and fluxes for steady-state conditions were numerically simulated (Matlab) and compared to the analytical data. It is mentioned that an acceptable agreement was reached.

Keywords: Biosensor, Carbon Nanotube. Akbari-Ganji method, Taylor's series, Ancient Chinese algorithms.

1. INTRODUCTION

Nanoelectrochemistry is a new multidisciplinary discipline of electrochemistry that studies the electrical and electrochemical properties of materials up to the nanoscale. Nanoelectrochemistry is also used to make a variety of biosensors and bioelectronics devices that can detect chemicals at deficient concentrations.

Carbon nanotubes (CNTs) have drawn attention in electrochemistry because of their size and

excellent electrochemical properties. There are many different types of carbon nanotubes, including single-walled, multi-walled and nitrogen-doped carbon nanotubes. Many industries use carbon nanotubes, including solar cells [1], electrochemical devices [2], hydrogen storage materials [3], field emission devices [4], carbon nanotube transistors [6], sensors and probes [7], pharmaceuticals [8], catalyst carriers [9], carbon-based electronics [10], and engineering materials [11].

The DFT was utilized by Fangfang et al. [12] to explore the physical assemblies and electrochemical properties of CNT's various components. Mirkin and Amemiya[13] discuss new obstacles and opportunities arising from nano electrochemical techniques. Gooding [14] discussed carbon nanotube nanostructuring electrodes. Baronas et al. [15] describe the mediator amperometric biosensors mathematical model. Lyons [16] proposed a unified model for describing substrate and redox mediator reaction kinetics and diffusion inside a scattered enzyme-loaded carbon nanotube film with a finite thickness. When the film is conducting and when the film is less conducting, approximate analytical expressions for the reaction flux are determined. Baronas et al. [17] solved a steady-state problem in a two-compartment domain. A mediated biosensor containing a carbon nanotube electrode was presented by Baronas et al. [17].

The mathematical solutions are numerical or approximate analytical, depending on the situation. This form of analysis has been detailed [18–20]. Albery and coworkers [21], Bartlett et al. [22], and others [23] contributed significant theoretical approaches on transport and kinetics in immobilized enzyme processes. Saveant and coworkers [24–26], Gooding et al. [30], Kulys and Baronas [29] and Lyons [16,27,28] have recently published comprehensive theoretical papers. Recently Kirthiga et al. [31] applied the new homotopy perturbation approach to solve the nonlinear system in amperometric biosensors. In the present communication, the new and straightforward closed-form of analytical expression is obtained using the Akbari-Ganji method and Taylor's series with ancient Chinese algorithm.

2. MATHEMATICAL FORMULATION OF THE PROBLEM

Electrochemical carbon nanotube (CNT) electrodes were made from single and double-walled carbon nanotubes. Figure 1 depicts a schematic illustration of substrate and mediator reaction and diffusion within an immobilised nanotube mesh. For the reduced form of substrate and redox mediator, the one-dimensional steady-state mass balance equations represented in normalized forms as follows (refer supplementary information)[31]:

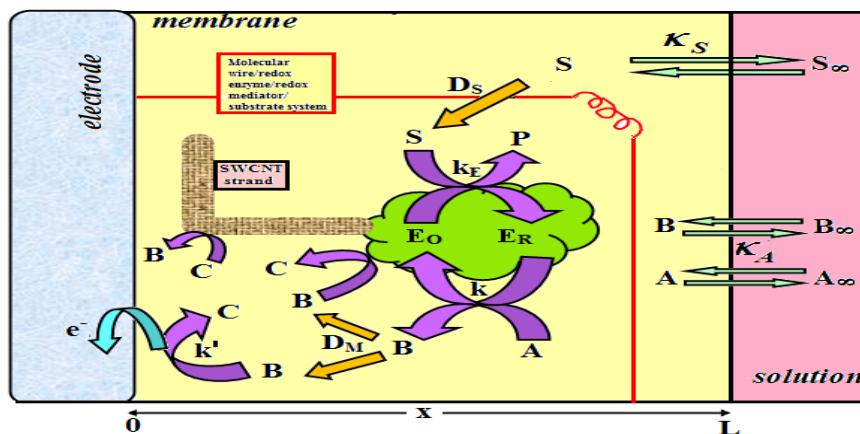


Figure 1. Schematic illustration of reaction and diffusion within an immobilised nanotube mesh [31]

$$\frac{d^2u(\chi)}{d\chi^2} - \frac{\gamma_S u(\chi)}{1 + (\alpha + k)u(\chi)} = 0 \tag{1}$$

$$\frac{d^2v(\chi)}{d\chi^2} + \frac{\gamma_M u(\chi)}{1 + (\alpha + k)u(\chi)} = 0 \tag{2}$$

The respective boundary conditions are

$$\frac{du}{d\chi} = 0, v = v_0 = \zeta^{-1} \left. \frac{dv(\chi)}{d\chi} \right|_{\chi=0} \text{ at } \chi = 0 \tag{3}$$

$$u = 1, v = 0 \text{ at } \chi = 1 \tag{4}$$

where $u(\chi)$ and $v(\chi)$ are the substrate and redox mediator concentrations, respectively. Saturation and kinetic competition parameters are denoted by α , and κ , while reaction diffusion parameters for substrate and redox mediator are denoted by γ_S and γ_M respectively. Nonlinear equations of these type can also be found in various fields of physical, chemical and biosensors [32]. Normalized substrate flux and net flux is given by [30] .

$$\psi_S = \frac{f_S}{f_{SD}} = \frac{f_S}{k_S D_S S^\infty / L} = \left(\frac{du}{d\chi} \right)_{\chi=1} \tag{5}$$

$$\psi_\Sigma = \left(\frac{dv}{d\chi} \right)_{\chi=0} \tag{6}$$

3. APPROXIMATE ANALYTICAL EXPRESSION OF SUBSTRATE AND REDOX MEDIATOR CONCENTRATION USING AKBARI GANJI METHOD

There are variety of asymptotic approaches are available for solving nonlinear differential equations. Such methods are Green’s function method [33–35], Homotopy perturbation method [36,37],

Variational iteration method [38–41], Akbari Ganji's method [42], Pade approximant method [43], Adomain decomposition method (ADM) [44–47], Taylor's series method [48–51], analytical methods [33,52,53].

This communication uses Akbari-Ganji's method which will acquire a solution with precision. Moreover, this method will be simple and convenient compared to the other methods. Solving the nonlinear equations (1-2) using the Akbari-Ganji method (Appendix A), the concentration of substrate and redox mediator are obtained as follows:

$$u(\chi) = \frac{\cosh(m\chi)}{\cosh m}, \quad (7)$$

$$v(\chi) = \frac{\mu}{m^2} \left[\cosh m - \cosh m \chi + \frac{\zeta(1 - \cosh m)}{\zeta + 1} (1 - \chi) \right] \quad (8)$$

$$\text{where } m = \sqrt{\frac{\gamma_S}{1+\alpha+\kappa}}, \quad \mu = \frac{\gamma_M}{(1+\alpha+\kappa) \cosh m} \quad (9)$$

Concentration of mediator related to substrate concentration is given as (Appendix B)

$$v(\chi) \approx v_0 \zeta (\chi - 1) + \frac{\gamma_M}{\gamma_S} [1 - u(\chi)] \quad (10)$$

Here v_0 is obtained from eq. (9) and (10)

$$v_0 = \frac{\mu \cosh m - 1}{m^2 (\zeta + 1)} \quad (11)$$

We get normalized substrate flux using Eq.(7) as follows:

$$\psi_S = m \tanh m \quad (12)$$

Using Eq.(8), normalized mediator flux can be obtained as

$$\psi_\Sigma = \left. \frac{dv(\chi)}{d\chi} \right|_{\chi=0} = v_0 \zeta = \frac{\mu}{m^2} \left[\frac{\cosh m - 1}{(1 + \zeta^{-1})} \right] \quad (13)$$

4. ANALYTICAL SOLUTION OF SUBSTRATE AND REDOX MEDIATOR USING TAYLOR'S SERIES AND YING BUZU CHINESE ALGORITHM.

There are no accurate solutions to the nonlinear systems (Eqns.(1)-(2)). In terms of the features of the controlling system, it was also suggested that approximate analytical approaches, rather than numerical ones, are more valuable. Using a new Taylor's series approach coupled with the ancient Ying Buzu Chinese algorithm, we achieve highly accurate and reliable approximation analytical results in this part.

In this study, an ancient Chinese algorithm [54] is used with Taylor's series method to solve boundary value problems (Eqs. (1-4)). Taylor's series approach is also used for solving linear problems in two and three independent variables for partial differential equations with constant coefficients and analytic initial conditions [48–51]. Nonlinear oscillators and fractal vibration systems [55–57] are now commonly solved using the Ying Buzu algorithm. The approximate solution for the concentration of the substrate and mediator using the Taylor's series method is as follows [Appendix A]:

$$u(\chi) \approx u(0) \left\{ 1 + \gamma_S \left[\frac{1}{1+(\alpha+k)u(0)} \frac{\chi^2}{2!} + \frac{\gamma_S}{(1+(\alpha+k)u(0))^3} \frac{\chi^4}{4!} - \frac{\gamma_S^2(6(\alpha+k)u(0)-1)}{(1+(\alpha+k)u(0))^5} \frac{\chi^6}{6!} \right] \right\} \tag{14}$$

$$v(\chi) \approx \frac{\gamma_M}{\gamma_S} [1 - u(\chi)] + v_0 \zeta (\chi - 1) \tag{15}$$

The dimensionless current is given by

$$\psi_S = \frac{du(\chi)}{d\chi} \Big|_{\chi=1} = u(0) \left\{ \gamma_S \left[\frac{1}{1+(\alpha+k)u(0)} + \frac{\gamma_S}{(1+(\alpha+k)u(0))^3} \frac{1}{6} - \frac{\gamma_S^2(6(\alpha+k)u(0)-1)}{(1+(\alpha+k)u(0))^5} \frac{1}{120} \right] \right\} \tag{16}$$

$$\psi_\Sigma = \frac{dv(\chi)}{d\chi} \Big|_{\chi=0} = v_0 \zeta \tag{17}$$

Using the boundary condition $\chi = 1, u = 1$ (eqn(4)), and the eqn.(14) we get

$$u(0) \left\{ 1 + \gamma_S \left[\frac{1}{1+(\alpha+k)u(0)} \frac{1}{2!} + \frac{\gamma_S}{(1+(\alpha+k)u(0))^3} \frac{1}{4!} - \frac{\gamma_S^2(6(\alpha+k)u(0)-1)}{(1+(\alpha+k)u(0))^5} \frac{1}{6!} \right] \right\} - 1 = 0 \tag{18}$$

The unknown parameter $u(0)$ in the above equation (18) for the given values of γ_S, α and κ can be obtained using the following Ying Buzu Chinese algorithm.

4.1 Basic Idea of Ying Buzu Chinese algorithm.

A brief introduction to the Ying Buzu algorithm is referred to Ref. [54], and it is now widely applied to solve nonlinear oscillators and fractal vibration systems [55–57]. Take the following algebraic equation.

$$f(x) = 0 \tag{19}$$

Let x_1 and x_2 be approximate solutions to the equation that yields in the remainders.

$f(x_1)$ and $f(x_2)$ respectively such that $f(x_1)$ and $f(x_2)$ have opposite signs. The enhanced approximate solution is

$$x_3 = \frac{x_2 f(x_1) - x_1 f(x_2)}{f(x_1) - f(x_2)}. \tag{20}$$

This iteration can be repeated to improve the accuracy of the solution.

4.2 Solution using Ying Buzu chinese algorithm

The eqn.(14) can be reduced as

$$f(x) = x \left\{ 1 + \gamma_S \left[\frac{1}{1+(\alpha+k)x} \frac{1}{2!} + \frac{\gamma_S}{(1+(\alpha+k)x)^3} \frac{1}{4!} - \frac{\gamma_S^2(6(\alpha+k)x-1)}{(1+(\alpha+k)x)^5} \frac{1}{6!} \right] \right\} - 1 = 0 \tag{21}$$

For the particular experimental values of the given parameter $\alpha = 0.1, k = 10$ and $\gamma_S = 5$ the above equation becomes

$$f(x) = x \left\{ 1 + 5 \left[\frac{1}{1+10.1x} \frac{1}{2!} + \frac{5}{(1+10.1x)^3} \frac{1}{4!} - \frac{25(60.6x-1)}{(1+10.1x)^5} \frac{1}{6!} \right] \right\} - 1 = 0 \tag{22}$$

Now assume that $x_1 = 0.15$ and $x_2 = 0.18$ be the approximation of above equation. Using these initial guesses with Eq. (23) leads to

$$f(x_1 = 0.7) = -0.0819, f(x_2 = 0.8) = 0.0212$$

Using Ying Buzu chinese algorithm, the improved approximate solution is

$$x_3 = \frac{x_2 f(x_1) - x_1 f(x_2)}{f(x_1) - f(x_2)} = \frac{0.8 (-0.0819) - 0.7 (0.0212)}{(-0.0819) - (0.0212)} = 0.779 \tag{23}$$

The solution of the equation (18) becomes

$$u(0) \approx 0.7794 \tag{24}$$

Now the substrate and product using eqn (14) and (15) becomes as follows:

$$u(\chi) \approx 0.7794 \left\{ 1 + 5 \left[\frac{1}{8.8719} \frac{\chi^2}{2!} + \frac{5}{(8.8719)^3} \frac{\chi^4}{4!} - \frac{25(46.2316)}{(8.8719)^5} \frac{\chi^6}{6!} \right] \right\} \tag{25}$$

$$= 0.7794 + 0.2192\chi^2 + 0.0011\chi^4 - 0.0001\chi^6$$

$$v(\chi) \approx \frac{\gamma_M}{\gamma_S} [1 - 0.7794 + 0.2192\chi^2 + 0.0011\chi^4 - 0.0001\chi^6] + v_0 \zeta (\chi - 1) \tag{26}$$

5. PREVIOUS ANALYTICAL EXPRESION OF CONCENTRAYION SUBSTRATE

Lyons et al. [58] has found analytical expression of the concertation of substrate for the limiting cases (Zero-order and First-order kinetics) as follows :

$$u(\chi) = \cosh(\sqrt{\gamma_S} \chi) / \cosh(\sqrt{\gamma_S})$$

(27)

when $\alpha + k \ll 1$.

$$u(\chi) = 1 + \frac{\gamma_S}{2\alpha} (\chi^2 - 1)$$

(28)

when $\alpha + k \gg 1$. This expression is valid for $\frac{\gamma_S}{2\alpha} < 1$.

6. NUMERICAL SIMULATION

The function pdex4 in SCILAB software, which solves the boundary value problems for differential equations, is used to solve equations (1) and (2). Upon comparison in the figures 2-4, it is evident that both the results give satisfactory agreement. The comparison between numerical results and the analytical result of the substrate obtained in this work and previous work by Lyons et al. [58] was shown in Tables 1 and 2. And the relative error percentage compared with numerical simulation is comparatively less for our result than the Albery result.

Table 1. Comparison of numerical solution of concentration $u(\chi)$ with the analytical solution of this work and Lyons et al. [58] work for limiting case $\alpha + k \ll 1$.

χ	$\kappa = 0.1, \alpha = 0.1, \gamma_S = 1$					$\kappa = 0.01, \alpha = 0.01, \gamma_S = 1$				
	NUM	This work	Lyons et al. [58]	This work	Lyons et al. [58]	NUM	This work	Lyons et al. [58]	This work	Lyons et al. [58]
		Eq. (7)	Eq. (27)	error %	error %		Eq. (7)	Eq. (27)	error %	error %
0.2	0.6929	0.7029	0.6611	1.4458	4.5954	0.6644	0.6658	0.6611	0.2056	0.5029
0.4	0.7294	0.7380	0.7006	1.1747	3.9493	0.7037	0.7048	0.7006	0.1569	0.4414
0.6	0.7913	0.7977	0.7682	0.8071	2.9135	0.7707	0.7716	0.7682	0.1132	0.3184
0.8	0.8806	0.8841	0.8667	0.3938	1.5750	0.8682	0.8687	0.8667	0.0573	0.1693
1.0	1.0000	1.0000	1.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000
	Average Error %			0.7643	2.6066	Average Error %			0.1066	0.2864

Table 2. Comparison of numerical solution of concentration $u(\chi)$ with the analytical solution of this work and Lyons et al. [58]work for limiting case $\alpha + k \gg 1$.

χ	$\kappa = 1, \alpha = 5, \gamma_S = 1$					$\kappa = 5, \alpha = 10, \gamma_S = 1$				
	NUM	This work	Lyons et al. [58]	This work	Lyons et al. [58]	NUM	This work	Lyons et al. [58]	This work	Lyons et al. [58]
		Eq. (7)	Eq. (28)	error %	error %		Eq. (7)	Eq. (28)	error %	error %
0.2	0.9320	0.9353	0.9040	0.3493	3.0043	0.9700	0.9708	0.9520	0.0779	1.8557
0.4	0.9405	0.9433	0.9160	0.2943	2.6050	0.9738	0.9744	0.9580	0.0611	1.6225
0.6	0.9547	0.9567	0.9360	0.2067	1.9587	0.9800	0.9805	0.9680	0.0481	1.2245
0.8	0.9745	0.9755	0.9640	0.1076	1.0775	0.9888	0.9890	0.9820	0.0201	0.6877
1.0	1.0000	1.0000	1.0000	0.2395	2.1614	1.0000	1.0000	1.0000	0.0000	0.0000
	Average Error %			0.2395	2.1614	Average Error %			0.0414	1.0781

7. DISCUSSION

Eqs. (8)–(9) are the new-form of analytical expression of concentration substrate and redox mediator for diverse values of constraints such as κ, α, γ_S and γ_M . Graphical representation of concentration versus distance illustrated in Figures 2-3 for the prescribed parameters. The influence of reaction-diffusion parameters for the dimensionless concentration $u(\chi)$ is shown in Fig. 2a. It is detected that the concentration $u(\chi)$ decreases when substrate reaction/diffusion parameter (γ_S) increases from these figures.

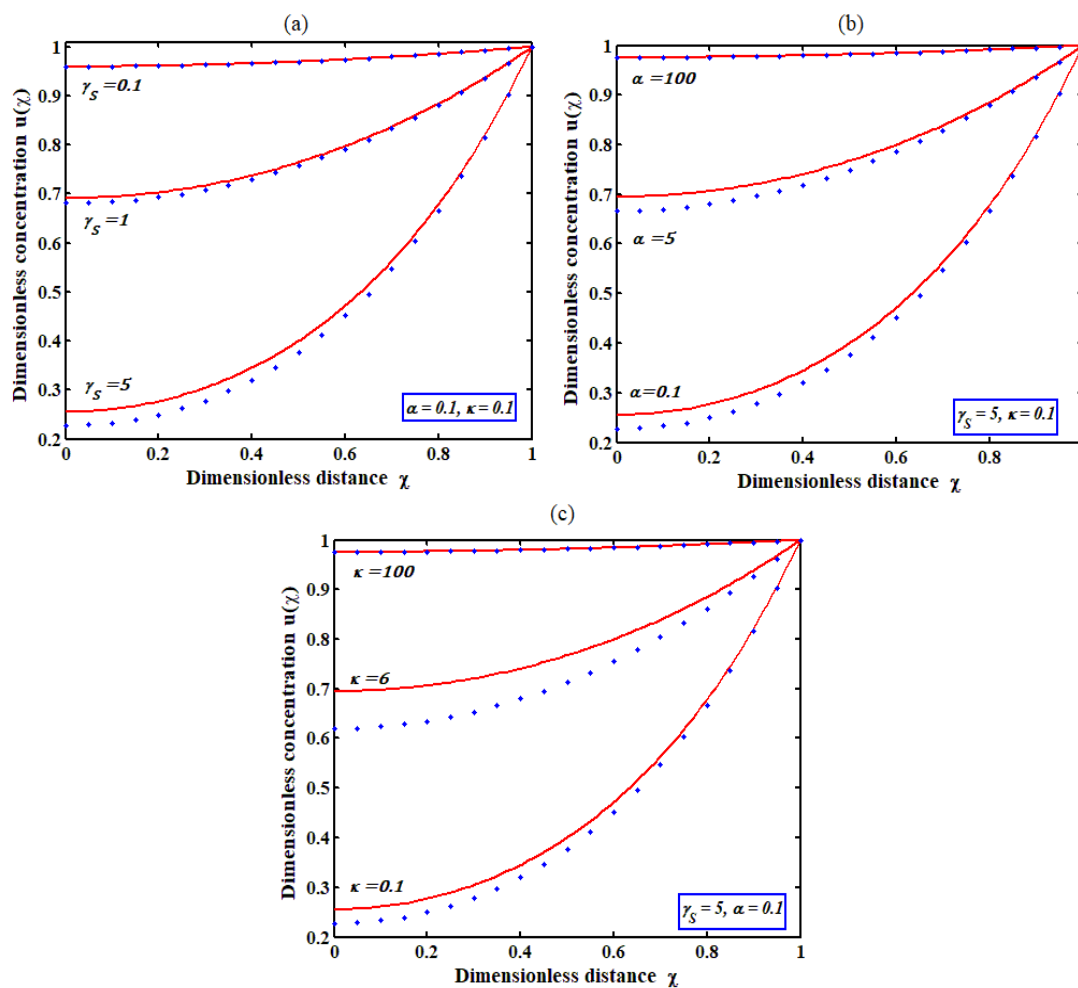


Figure 2. Dimensionless concentration of substrate versus dimensionless distance for various values κ . The spotted line represents simulation solution and solid line obtained using Eq.(7).

The effect of saturation parameter (α), kinetic competition parameter (κ) on substrate concentration is shown in Fig. 2b and Fig.2c, and the result depicted that the substrate $u(\chi)$ decreases for the decreasing values of α and κ . The increasing values of γ_S, α, κ and ζ results on decreases in the mediator concentration, which is observed from Figs. 3a,3c,3d and 3e. Fig.3b shows that the mediator concentration increases when mediator reaction/diffusion parameters γ_M decrease.

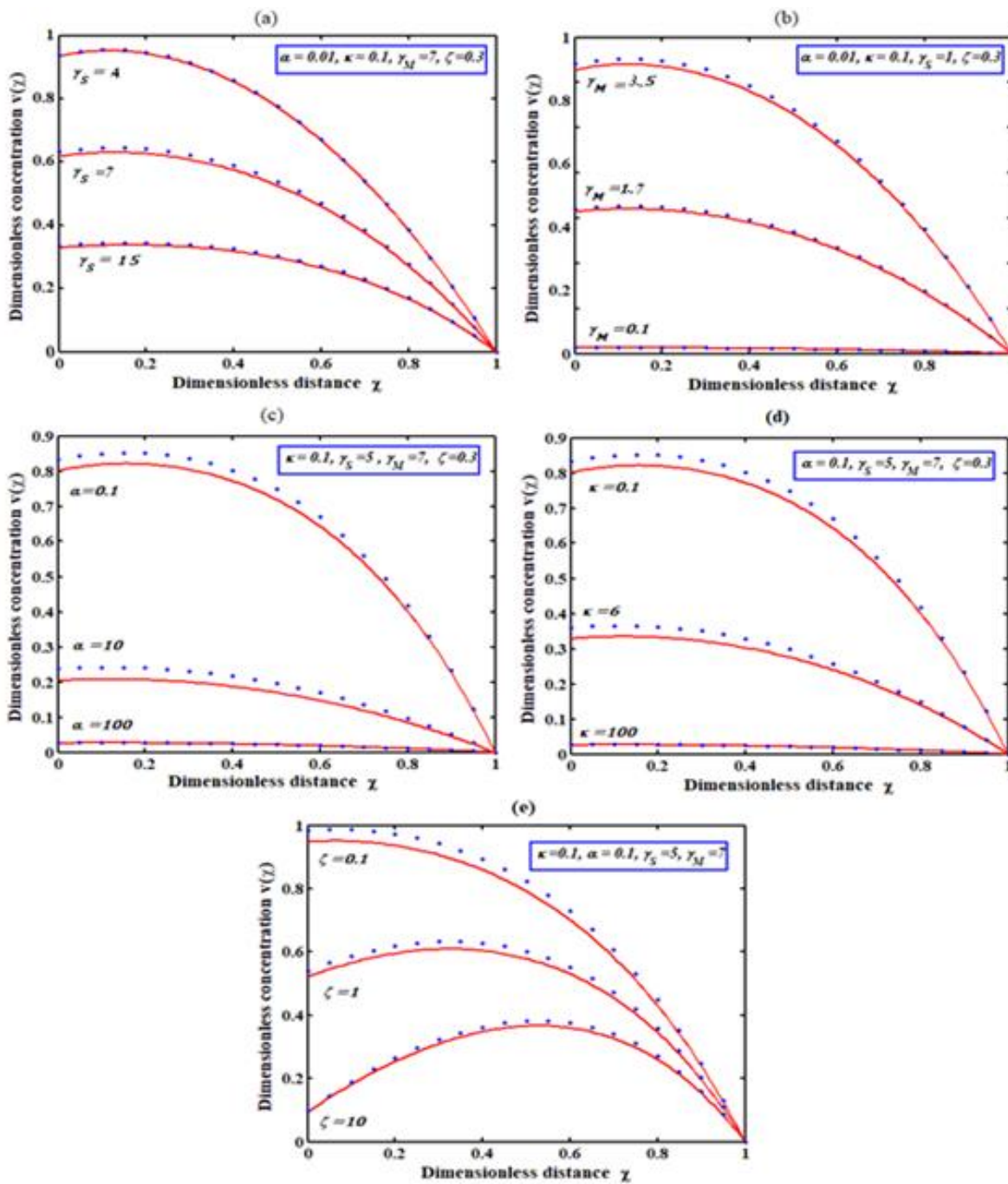


Figure 3. Dimensionless concentration of mediator versus dimensionless distance for various values $\gamma_S, \gamma_M, \alpha, \kappa$ and ζ . The spotted line represents simulation solution and solid line obtained using Eq.(8).

The graphical model of flux ψ_Σ versus electrode potential is given in Figure 4 which shows that the mediator flux rises as the potential rises. Flux progressively grows from zero and grasps the extreme value when $\zeta \approx 20$. The highest range of the flux rises when γ_S, κ and α declines or γ_M rises .

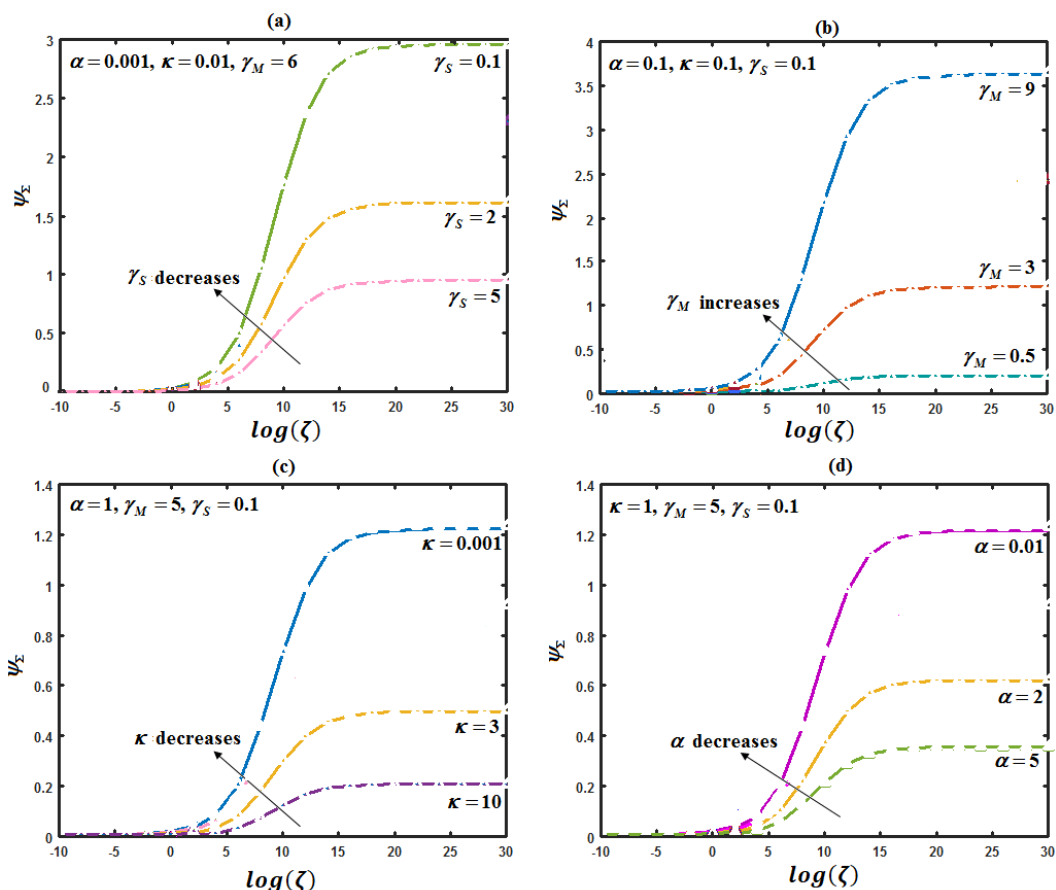


Figure 4. Normalized mediator flux against potential. Spotted line represents simulation solution and the solid line represent analytical solution. The values used are $D_M = 10^{-3}, L = 1, k_0 = 0.1, \beta = 0.5$.

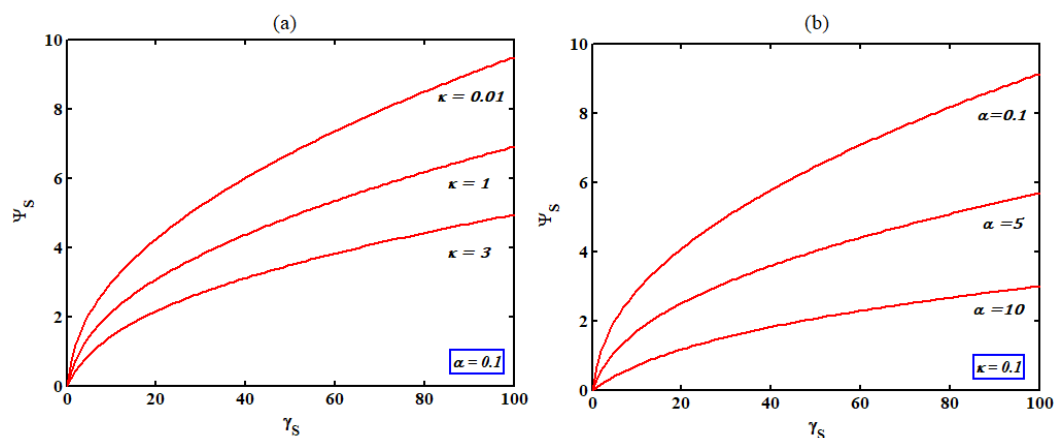


Figure 5. Plot of normalized substrate flux ψ_S versus substrate diffusion parameter γ_S using Eq. (12)

Fig. 5 is the graphical representation of normalized substrate flux against versus substrate diffusion parameter for the various values of α, κ . Substrate flux increases as the diffusion parameter increases. However, as the saturation and kinetic parameter decreases, the total current increases.

8. CONCLUSIONS

A one-dimensional theoretical model is used to analyse the reaction and transport of substrate and redox mediator in carbon nanotubes is discussed using a one-dimensional theoretical model. The Akbari-Ganji approach and Taylor's series with Chinese algorithms were applied to unravel time-independent equation system. The derived analytical solutions were compared to numerical results, and there was a good agreement. The influence of several fundamental kinetic parameters on substrate, mediator concentration and current are discussed.

Appendix A. Analytical solution of equations (1) using Akbari-Ganji method

Consider the equation (1) as follows:

$$\frac{d^2u(\chi)}{d\chi^2} - \frac{\gamma_s u(\chi)}{1 + (\alpha + k)u(\chi)} = 0 \quad (\text{A. 1})$$

The boundary conditions are

$$\text{At } \chi = 0, \frac{du}{d\chi} = 0; \quad \text{At } \chi = 1, u = 1 \quad (\text{A. 2})$$

Let the following hyperbolic function be the approximate trial solution of $u(\chi)$

$$u(\chi) = A \cosh(m\chi) + B \sinh(m\chi), \quad (\text{A. 3})$$

where A, B , and b are constants. From boundary condition (A.2), we find that

$$A = \frac{1}{\cosh m} \text{ and } B = 0. \quad (\text{A. 4})$$

Therefore Eq. (A.3) becomes

$$u(\chi) = \frac{\cosh(m\chi)}{\cosh m}, \quad (\text{A. 5})$$

Substituting Eq. (A.5) into (A.1) gives

$$m^2 \frac{\cosh(m\chi)}{\cosh m} - \frac{\gamma_s \cosh(m\chi)}{\cosh m + (\alpha + k) \cosh(m\chi)} = 0. \quad (\text{A. 6})$$

By substituting $\chi = 1$ into (A.6) we get

$$m = \sqrt{\frac{\gamma_s}{1 + \alpha + k}} \quad (\text{A. 7})$$

Equation (A.7) can be used to find m for any given numerical values of γ_s, α and k .

Appendix B. Analytical solution of nonlinear equations using Taylor's series method

The Maclaurin series (Taylor's series at $\chi = 0$) expansion for $u(\chi)$ is

$$u(\chi) = \sum_{q=0}^r \left(\frac{d^q u}{d\chi^q} \Big|_{\chi=0} \right) \frac{\chi^q}{q!}. \quad (\text{B. 1})$$

Assume that $\left. \frac{d^q u}{d\chi^q} \right|_{\xi=0} = A_q$ and $\left. \frac{d^q v}{d\chi^q} \right|_{\xi=0} = B_q$.

Now eqn. (B.1) can be written as

$$u(\chi) = \sum_{q=0}^r A_q \frac{\chi^q}{q!}. \quad (\text{B. 2})$$

As consequence of Eq. (B.1), we obtain

$$A_0 = u(0), A_1 = 0, A_2 = \frac{\gamma_S u(0)}{1+(\alpha+k)u(0)}, A_3 = 0, A_4 = \frac{\gamma_S^2 u(0)}{(1+(\alpha+k)u(0))^3}, A_5 = 0, A_6 = -\frac{\gamma_S^3 u(0)(6(\alpha+k)u(0)-1)}{(1+(\alpha+k)u(0))^5} \quad (\text{B. 3})$$

Using Eqs. (B.3) in Eq. (B.2) leads to the analytical expression

$$u(\chi) \approx u(0) \left\{ 1 + \gamma_S \left[\frac{1}{1+(\alpha+k)u(0)} \frac{\chi^2}{2!} + \frac{\gamma_S}{(1+(\alpha+k)u(0))^3} \frac{\chi^4}{4!} - \frac{\gamma_S^2(6(\alpha+k)u(0)-1)}{(1+(\alpha+k)u(0))^5} \frac{\chi^6}{6!} \right] \right\} \quad (\text{B. 4})$$

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Supplementary Information

Appendix C: Mathematical formulation of the problem:

The reaction sequences in term of the ping-pong mechanism is described as [16]



where S, P represent the substrate and product species respectively. E_o, E_R denote the oxidized and reduced forms of the redox enzyme and A, B denote the oxidized (MO) and reduced (MR) forms of the redox mediator respectively.

The nonlinear reaction diffusion equation for concentration of substrate and reduced mediator are given as

$$D_s \frac{d^2 s}{dx^2} - \frac{k_a k_c e_{\Sigma} s}{k_a(s+K_m) + k_c s} = 0 \tag{C.5}$$

$$D_B \frac{d^2 b}{dx^2} + \frac{k_a k_c e_{\Sigma} s}{k_a(s+K_m) + k_c s} = 0 \tag{C.6}$$

where $s(x)$ and $b(x)$ denote the concentration of substrate and oxidised mediator, D_s and D_b , are the diffusion coefficient of substrate and mediator respectively. k_a , k_c and K_m denote catalytic constants and Michaelis constant for the immobilized redox enzyme e_{Σ} is the total enzyme concentration. This equation must be solved subject to the following boundary conditions.

$$\text{At } x = 0, \frac{ds}{dx} = 0; b = b_0 = f_{\Sigma} / \kappa \text{ where } f'_{\Sigma} = f_s = D_B \left(\frac{ds}{dx} \right)_{x=0} \tag{C.7}$$

$$\text{At } x = L, s = K_s s^{\infty}; b = 0 \tag{C.8}$$

Units of the parameters are given in (Nomenclature) [31]. By defining the following dimensionless parameter

$$\chi = \frac{x}{L}, u = \frac{s}{K_s s^{\infty}}, v = \frac{b}{K_s s^{\infty}}, \gamma_s = \frac{\left(\frac{k_c}{K_m} \right) e_{\Sigma} L K_s s^{\infty}}{D_s K_s s^{\infty}}, \gamma_M = \frac{\left(\frac{k_c}{K_m} \right) e_{\Sigma} L K_s s^{\infty}}{D_M K_A s^{\infty}},$$

$$k = \frac{\left(\frac{k_c}{K_m} \right) e_{\Sigma} L K_s s^{\infty}}{\kappa e_{\Sigma} L k_a a^{\infty}}, \alpha = \frac{K_s s^{\infty}}{K_m}, \zeta = \frac{\left(\exp\left(\frac{\beta F}{RT} (E - E^0) \right) \right) L}{D_M} \tag{C.9}$$

we get the dimensionless Eq.(1) and Eq.(2) in the text.

Appendix D: General relation between concentration of substrate and mediator.

By count Eq.1 and Eq.2 we get

$$\frac{d^2v}{d\chi^2} = -\frac{\gamma_M}{\gamma_S} \left(\frac{d^2u}{d\chi^2} \right) \tag{D. 1}$$

Integrating on both sides we get

$$\frac{dv}{d\chi} = -\frac{\gamma_M}{\gamma_S} \left(\frac{du}{d\chi} \right) + C_1 \tag{D. 2}$$

Using the boundary conditions Eq.3 we get

$$\frac{dv}{d\chi} = -\frac{\gamma_M}{\gamma_S} \left(\frac{du}{d\chi} \right) + v_0\zeta \tag{D. 3}$$

Again integrating the above equation we obtain

$$v(\chi) = -\frac{\gamma_M}{\gamma_S} u(\chi) + v_0\zeta\chi + C_2 \tag{D. 4}$$

Using the boundary condition Eq.4 we find

$$v(\chi) \approx v_0\zeta(\chi - 1) + \frac{\gamma_M}{\gamma_S} [1 - u(\chi)] \tag{D. 5}$$

Another way of finding the relationship is as follows

Now the Eq. (2) can be written as

$$\frac{d^2v(\chi)}{d\chi^2} + \frac{\gamma_S u(\chi)}{1 + (\alpha + k)u(\chi)} = 0 \tag{D. 6}$$

$$\frac{d^2v(\chi)}{d\chi^2} + \frac{\gamma_S u(\chi)}{1 + (\alpha + k)u(\chi = 1)} = 0 \tag{D. 7}$$

Substituting the value of $u(\chi)$ (obtained in Appendix A) (A.5) in (D.7)

$$\frac{d^2v(\chi)}{d\chi^2} + \frac{\gamma_M}{1 + (\alpha + k)} \left(\frac{\cosh m\chi}{\cosh m} \right) = 0 \tag{D. 8}$$

Boundary conditions are

$$\text{when } \chi = 0, v = v_0 = \zeta^{-1} \left. \frac{dv}{dx} \right|_{x=0} \tag{D. 9}$$

$$\text{when } \chi = 1, v = 0 \tag{D. 10}$$

Solving Eq. (D.6) we get

$$v(\chi) = -\frac{\mu}{m^2} \cosh m \chi + \chi c_2 + c_1 \tag{D. 11}$$

$$v(\chi)|_{\chi=0} = -\frac{\mu}{m^2} + c_1 = v_0 \tag{D. 12}$$

$$\frac{dv(\chi)}{d\chi} = -\frac{\mu}{m} \sinh m \chi + c_2 \tag{D. 13}$$

$$\left. \frac{dv(\chi)}{d\chi} \right|_{\chi=0} = c_2 = v_0 \zeta \tag{D. 14}$$

When $\chi = 1$, using equation (D.10) in (D.11) we get

$$c_2 + c_1 = \frac{\mu}{m^2} \cosh m \tag{D. 15}$$

From equations (D.12) and (D.14) we get

$$c_1 - \zeta^{-1} c_2 = \frac{\mu}{m^2} \tag{D. 16}$$

Solving (D.15) and (D.16) we get

$$c_1 = \frac{\mu}{m^2} \left[\cosh m - \frac{\cosh m - 1}{(1 + \zeta^{-1})} \right], c_2 = \frac{\mu}{m^2} \frac{\cosh m - 1}{(1 + \zeta^{-1})}, v_0 = \frac{\mu}{m^2} \frac{\cosh m - 1}{(1 + \zeta)} \tag{D. 17}$$

Substituting above values in (D.11), we obtain Eq.(8)

$$v(\chi) = \frac{\mu}{m^2} \left[\cosh m - \cosh m \chi + \frac{\zeta(1 - \cosh m)}{\zeta + 1} (1 - \chi) \right] \tag{D. 18}$$

here $m = \sqrt{\frac{\gamma_S}{1 + \alpha + \kappa}}, \mu = \frac{\gamma_M}{(1 + \alpha + \kappa) \cosh m} \tag{D. 19}$